



**Europäisches
Patentamt**

**European
Patent Office**

PCT/EP200 4 / 0 5 3 3 5 7
**Office européen
des brevets** 08.12.04

Bescheinigung

Certificate

Attestation

Die angehefteten Unterla-
gen stimmen mit der
ursprünglich eingereichten
Fassung der auf dem näch-
sten Blatt bezeichneten
europäischen Patentanmel-
dung überein.

The attached documents
are exact copies of the
European patent application
described on the following
page, as originally filed.

Les documents fixés à
cette attestation sont
conformes à la version
initialement déposée de
la demande de brevet
européen spécifiée à la
page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

03257777.7

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk

BEST AVAILABLE COPY



Europäisches
Patentamt

European
Patent Office

Office européen
des brevets

PCT/EP2004/053357

08.12.07

Anmeldung Nr.:
Application no.: 03257777.7
Demande no:

Anmeldetag:
Date of filing: 10.12.03
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

SHELL INTERNATIONALE RESEARCH
MAATSCHAPPIJ B.V.
Carel van Bylandtlaan 30
2596 HR Den Haag
PAYS-BAS

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se référer à la description.)

Sulphur pellets containing H₂S suppressant

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s)
revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

C08K3/00

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL
PT RO SE SI SK TR LI

1
10 DEC 200

LONDON

TS 9512 EPC

Iye

SULPHUR PELLETS CONTAINING H₂S-SUPPRESSANT

FIELD OF THE INVENTION

The invention relates to sulphur pellets. The invention further relates to a process for the manufacture of sulphur pellets. The invention further relates to a process for the manufacture of a sulphur-containing asphalt paving mixture using sulphur pellets. The invention also relates to the use of a sulphur-containing asphalt paving mixture in the paving of roads.

BACKGROUND OF THE INVENTION

In the road construction and road paving industry, it is a well-practised procedure to coat aggregate material such as sand, gravel, crushed stone or mixtures thereof, with hot fluid bitumen, spread the coated material as a uniform layer on a road bed or previously built road while it is still hot, and compact the uniform layer by rolling with heavy rollers to form a smooth surfaced road. The term "asphalt" as used herein refers to the combination of bitumen with aggregate material, such as sand, gravel, crushed stone or mixtures thereof. The term "asphalt binder" as used herein refers to bitumen, usually a liquid binder comprising asphaltenes, resins and solvents. Bitumen can for example comprise pyrogenous mixtures derived from petroleum residues such as residual oils, tar or pitch or mixtures thereof.

It is known in the art that sulphur can be mixed with bitumen for applications in the road construction and road paving industry. Efforts towards improving bitumen are for example described in GB 1,528,384. More recently, studies on the use of sulphur in bituminous mixtures have indicated that the use of sulphur-containing asphalt

binders is feasible. Sulphur-containing asphalt binders are formulated by replacing some of the bitumen in conventional binders by sulphur.

One of the problems encountered when using sulphur in bitumen is the unwanted formation of H_2S , resulting from dehydrogenation reactions between bitumen and sulphur at high temperatures.

Even low H_2S emission from sulphur-containing asphalt mixtures presents an emission nuisance on road paving projects. This is due to the gradual H_2S gas concentration increase to high levels in the air voids in the loose paving mixture during storage in silos and during truck delivery to the paving site. The "stored" gas is released when the air pockets in the mixture are opened up as the mixture is dumped from the delivery trucks or as the mixture is "opened up" by mixing.

In view of the substantial amounts of sulphur used, especially in sulphur-containing asphalt having high sulphur-bitumen weight ratios, e.g. as high as 1:1, H_2S emission is a serious problem. Therefore, it is necessary to reduce the unwanted formation and emission of H_2S , especially from sulphur-containing asphalt.

One method to reduce H_2S -emission from hot cast sulphur-asphalt mixtures is to add H_2S -suppressants in the process to manufacture sulphur-bitumen mixtures by mixing and heating sulphur and bitumen in the presence of added H_2S -suppressant as described in US 3,960,585.

A disadvantage of the method described in US 3,960,585 is that liquid H_2S -suppressant has to be injected into paving mixture at the mixing plant. Consequently, equipment for injecting has to be set up and maintained at the mixing plant, making the process

cumbersome and costly. In addition, it is more difficult to achieve a homogeneous distribution of H_2S -suppressant in the paving mixture.

5 It has now been found that a sulphur pellets containing H_2S -suppressant can be successfully used in a process for the manufacture of a sulphur-containing asphalt paving mixture.

SUMMARY OF THE INVENTION

10 The invention provides sulphur pellets containing at least one H_2S -suppressant. The invention further provides a process for the manufacture of sulphur pellets containing at least one H_2S -suppressant.

15 The invention further provides a process for the manufacture of a sulphur-containing asphalt paving mixture using H_2S -suppressant containing sulphur pellets according to the invention.

The invention also provides the use of a sulphur-containing asphalt paving mixture comprising H_2S -suppressant in the paving of roads.

20 DETAILED DESCRIPTION OF THE INVENTION

The invention provides sulphur pellets containing at least one H_2S -suppressant. Reference herein to pellets is to any type of formed sulphur, for example sphere shaped or half pea sized sulphur. Reference herein to a H_2S -
25 suppressant is to a compound capable of either suppressing the formation or emission of H_2S . Typically, H_2S -suppressants are one or more compounds selected from the class of free radical inhibitors and redox catalysts. Preferably, H_2S -suppressants are selected from the group
30 of tetra-alkyl-thiuram disulfide, dithiocarbamates, especially zinc dialkyl dithiocarbamates, amine compounds, iodine, copper salts, copper oxides, cobalt salts, cobalt oxides, iron oxides and iron salts. Preferred iron salts are iron chloride compounds, in

particular those iron chloride compounds selected from the group of ferric chloride, hydrated ferric chloride, ferrous chloride and hydrated ferrous chloride. Hydrated ferrous chloride is the most preferred, because of its greater effectiveness as a H_2S -suppressant and because of its non-corrosivity.

The sulphur pellets containing H_2S -suppressant according to the invention typically comprise H_2S -suppressant in amounts between 0.02% and 10% (w/w), preferably between 0.05% and 6.5%, more preferably between 0.1% and 2.0%, based on the total pellet.

The use of sulphur pellets containing H_2S -suppressant eliminates the need for the installation and maintenance of injecting equipment at the asphalt mixing plant, thereby offering advantages compared with the process wherein H_2S -suppressants are added separately. Another advantage is that the sulphur pellets containing H_2S -suppressant according to the invention may help to prevent the detachment of bitumen film, the so-called "stripping", from water-sensitive mineral aggregates. This is especially important when hydrated lime is added to asphalt mixtures. The addition of hydrated lime to asphalt mixtures is beneficial because it reacts with bitumen, thereby removing oxygen-containing bitumen components and forming a strong bond. In sulphur containing asphalt mixtures however, the addition of hydrated lime causes problems. Some of the lime may be in the CaO state and a reaction with sulphur can take place to form synthetic gypsum. This synthetic gypsum is water-soluble and can cause sulphur-asphalt disintegration in the presence of water. The H_2S -suppressant containing sulphur-pellets according to the invention solve this problem as the H_2S -suppressant delays asphalt disintegrating and can prevent disintegrating from

mineral aggregates. Another advantage of the sulphur- pellets according to the invention is that because the H_2S -suppressant is incorporated in the sulphur pellet, the H_2S -suppressant will be in the vicinity of the sulphur in the final asphalt mixture, thereby being able to suppress the formation of H_2S evolving from the sulphur before the H_2S is released.

The invention further provides a process for the manufacture of sulphur pellets containing at least one H_2S -suppressant. In step (a) of the process for the manufacture of H_2S -suppressant-containing sulphur pellets according to the invention, elemental sulphur is mixed with one or more H_2S -suppressants and optionally a filler in a mixing unit to obtain a mixture.

Preferred H_2S -suppressants are compounds selected from the class of free radical inhibitors and redox catalysts as hereinbefore described. Preferably, the H_2S -suppressant is added as a solution in a suitable solvent, more preferably as a concentrated solution in a suitable solvent. Typically, the solvent is water. Typically, the H_2S -suppressant solution is introduced by pumping the solution from a reservoir unit into the mixing unit.

Typically, the mixing takes place at atmospheric pressure and at elevated temperatures. The mixing can take place at temperatures between 100 °C and 130 °C, preferably between 115 °C and 121 °C or at least 113 °C.

Elemental sulphur can be introduced into the mixing unit in many ways. Suitably it may be added as sulphur powder, or as a flow of molten sulphur or as a slurry of water and sulphur particles.

In a preferred process, the elemental sulphur is introduced as a slurry of water and sulphur particles. Typically, the sulphur particles are dispersed or suspended in the slurry. Preferably, the particles have a

size ranging from between about 0.5 to about 150 microns, preferably between about 1.0 and about 100 microns. To avoid the removal of excess water at a later stage in the process, the water content in the sulphur slurry is typically kept as low as possible, preferably between approximately 10 and 40% based on the total weight of the mixture, more preferably between 15 and 30% based on the total weight of the slurry. In the case where the sulphur particles are suspended in the slurry, the sulphur slurry is preferably stirred or mixed in a suitable apparatus to homogenise the slurry prior to introducing it into the manufacturing process. In a preferred embodiment, the sulphur slurry contains sulphur particles which are dispersed in the water. This type of slurry, henceforth referred to as dispersed or emulsified sulphur slurry, comprises dispersed sulphur particles in water, preferably dispersed micron-sized sulphur particles in water. The sulphur particles are suitably kept in dispersion through the addition of a suitable emulsifier. Suitable emulsifiers are known in the art and are not critical to the invention. An advantage of using dispersed sulphur particles is that the precipitation of sulphur particles is kept to a minimum and the sulphur is distributed more homogeneously throughout the water. Thus, the need for stirring or mixing prior to introducing the sulphur slurry into the reactor unit is reduced. Typically, the slurry is introduced by pumping the slurry from a sulphur slurry reservoir unit into the reactor unit. Preferably, the slurry is stirred or mixed in a suitable apparatus before it is introduced into the mixing unit of step (a).

In yet another preferred process according to the invention, the elemental sulphur is introduced into the

reactor unit in step (a) as molten sulphur. Molten sulphur can be obtained from solid sulphur, by melting in a suitable melting apparatus, for instance a tube melter. The use of molten sulphur is advantageous when sulphur is obtained in the molten state from an industrial process. Processes for the removal of unwanted sulphur components from natural gas usually produce sulphur in the molten state and the use of this molten sulphur directly in the sulphur pellet producing process avoids the need for additional steps, such as drying and grinding of the sulphur, to obtain a sulphur slurry. An additional advantage of using molten sulphur is that no additional water is introduced into the process. When adding elemental sulphur in the molten state, the temperature of the sulphur-containing mixture is preferably kept above the melting point of sulphur, preferably between temperatures of 115 °C and 121 °C.

In another preferred process according to the invention, biologically produced elemental sulphur is used. Reference herein to biologically produced elemental sulphur is to sulphur obtained from a process wherein sulphur-containing components, such as sulphides or H_2S , are converted to elemental sulphur via biological conversion. Biological conversion can suitably be effected using sulphide-oxidising bacteria. Suitable sulphide-oxidising bacteria can be selected for instance from the known autotrophic aerobic cultures of the genera *Thiobacillus* and *Thiomicrospira*. An example of a suitable biological conversion process to obtain the biologically produced elemental sulphur suitable for the process according to the invention is the process for the removal of sulphur compounds from gases wherein the gas is washed with an aqueous washing liquid and the washing liquid is

subjected to sulphide-oxidising bacteria, as described in WO 92/10270. Biologically produced elemental sulphur has a hydrophilic nature. An advantage of biologically produced elemental sulphur is that fouling or blocking of equipment is substantially reduced or even eliminated due to the hydrophilic nature. The biologically produced elemental sulphur can be introduced into the process as solid sulphur, as a slurry (including dispersed or emulsified sulphur) or as molten sulphur.

To achieve a more homogeneous distribution of the H_2S -suppressant throughout the sulphur, the H_2S -suppressant and the elemental sulphur are preferably premixed and introduced as a slurry or as a liquid into the mixing unit of step (a).

Optionally, a filler can be added in step (a). Suitable fillers include mineral fillers, such as calcium-based mineral fillers (for example calcium hydroxide). The addition of mineral fillers enables the use of a smaller quantity of sulphur and helps to improve the temperature-stability of the pellets.

After step (a), a mixture comprising sulphur and H_2S -supressant is obtained. This mixture is shaped and/or pettelised in a pelletising unit in step (b) to obtain H_2S -suppressant containing pellets. Suitable pelletising units are units for the formation of granules or pellets as described in Perry's Chemical Engineers' Handbook, chapter 20 (1997) or units wherein a liquid mixture comprising sulphur can be sprayed or poured onto a surface so that sulphur pellets are formed after cooling, for example as described in US 4,081,500 or US 4,043,717. The pelletising unit can suitably be a granulator, preferably a drum granulator.

In a preferred process, the mixture comprising sulphur and H_2S -supressant is liquid, the elemental sulphur being in the molten state. In a preferred

embodiment, the pelletising is done by forming droplets of the liquid mixture comprising sulphur and H_2S -supressant and depositing these droplets onto a suitable means for transporting, for example a conveyor belt.

5 Suitable, the liquid mixture is sprayed onto a conveyor belt through a spray head. After cooling, the droplets form into pellets.

10 Optionally, H_2S -suppressant-containing sulphur pellets obtained from step (b) are dried, suitably air-dried or dried in a drying unit. Suitable drying units include drying units wherein heat transfer for drying is accomplished by direct contact between the wet solid and hot gases. Typically, the drying unit is a rotary dryer.

15 The invention also provides a process to manufacture a sulphur-containing bitumen-aggregate mixture. In step (i) of this process bitumen is heated, typically at a temperature of between 120 and 180°C, preferably between 130 and 150 °C, more preferably between 140 and 150 °C. In step (ii) of this process aggregate is heated,
20 typically at a temperature of between 120 and 180°C, preferably between 130 and 150 °C, more preferably between 140 and 150 °C

25 In step (iii), the hot bitumen and aggregate are mixed in a mixing unit. Typically, the mixing takes place at a temperature of between 120 and 180°C, preferably between 130 and 150 °C, more preferably between 140 and 150 °C. Typically, the mixing time is between 10 and 60 seconds, preferably between 20 and 40 seconds. In the process according to the invention,
30 sulphur pellets containing H_2S -suppressant are added in step (i) or in step (ii) or in step (iii). Preferably, the addition of sulphur pellets containing H_2S -suppressant is followed by mixing for an additional time. Preferably, the additional mixing time is
35 between 10 and 60 seconds.

 In a preferred embodiment, aggregate is mixed with

H₂S-suppressant containing sulphur pellets. Bitumen is then added to the resulting aggregate-sulphur mixture.

In another preferred embodiment, aggregate is mixed with bitumen and the H₂S-suppressant containing sulphur pellets are added to the resulting bitumen-aggregate mixture. This embodiment offers the advantage of producing a stronger sulphur-asphalt mix strength.

In yet another preferred embodiment, bitumen is mixed with H₂S-suppressant containing sulphur pellets and the resulting bitumen-sulphur mixture is mixed with aggregate.

Typically, the amount of sulphur pellets containing H₂S-suppressant added to the bitumen-aggregate mixture is such, that a mixture comprising sulphur and bitumen in a weight ratio from about 1:0.5 to 1:5, preferably from about 1:1 to 1:4, is obtained. Typically, in the bitumen/aggregate mixture, at least 2% of bitumen is present, based on the total weight of the mixture. Mixtures containing from about 1% to about 10% of bitumen are preferred, with a special preference for mixtures containing from about 3% to about 6% of bitumen based on the total weight of the mixture.

The sulphur-containing asphalt paving mixture thus obtained can be used in the paving of roads, for example by applying it to the road with a paving machine, typically followed by roller compaction until the required density has been reached.

EXAMPLE 1 (comparative)

A mixture was prepared with the following procedure. Aggregate and bitumen were heated in an oven to 165 °C. The bitumen was added to the aggregate and mixed for 30 seconds in a Hobart mixer. Elemental sulphur pastilles without added H₂S suppressant were added and mixed for an additional 150 seconds. The temperature of the mixture was approximately 145 °C after mixing.

Approximately 3700 grams of mixture, with the following composition: Aggregate: 3535 g; bitumen: 132 g (3.5%); elemental sulphur: 87 g (2.3%), were then poured into a thermostatically controlled heated vessel.

5 H₂S concentrations in the vessel were measured periodically, approximately 30 mm above the surface of the mixture, with a gas meter with a built-in pump for drawing the H₂S gas into the meter. Measurements were done (a) after initial mixing and at various time periods
10 subsequently, after sulphur-containing asphalt re-mixing manually with the vessel cover removed and (b) after various time periods with the cover placed on the vessel, to force the gas concentration to accumulate within the vessel.

15 The mixture was stirred thoroughly from time-to-time and then a cover was placed on the vessel for a short period of time, typically 5 minutes, to allow the H₂S gas to accumulate inside the vessel. The H₂S concentration was then measured at 5 minute intervals. The H₂S
20 concentration was found to be 37 ppm after 5 minutes, at a mix temperature of 145 °C.

EXAMPLE 2 (according to the invention)

A mixture was prepared using the procedure described in the comparative example, except that H₂S-suppressant containing sulphur pellets, with a H₂S-suppressant concentration of 6.5% based on the total pellet, were used.

The resulting mixture had the following composition: Aggregate: 3535 g; bitumen: 132 g (3.5% based on total mix weight); elemental sulphur: 87 g (2.3% based on total mix weight), plus 6 g ferric chloride (hydrated weight 20 g). The H₂S concentration was found to be between 14 and 20 ppm after 5 minutes at a mix

temperature of 149 °C.

The results clearly show that the use of sulphur pellets containing H₂S suppressant results in a substantial decrease of H₂S formation.



C L A I M S

1. Sulphur pellets containing at least one H₂S-suppressant.

2. Sulphur pellets according to claim 1, wherein the H₂S-suppressant is one or more compounds selected from the class of free radical inhibitors and redox catalysts.

3. Sulphur pellets according to claim 1 or 2, wherein the H₂S-suppressant is selected from the group of iodine, amine compounds, copper salts, copper oxides, iron salts, iron oxides, cobalt salts and cobalt oxides.

4. Sulphur pellets according to claim 3, wherein the iron salts are iron chloride compounds, preferably selected from the group of ferric chloride, hydrated ferric chloride, ferrous chloride and hydrated ferrous chloride.

5. Sulphur pellets according to any one of claims 1 to 4, wherein the H₂S-suppressant is present in amounts between 0.025% and 5% (w/w), preferably between 0.05% and 2.5%, more preferably between 0.1% and 1.0%, based on the sulphur pellet.

6. A process for the manufacture of sulphur pellets containing at least one H₂S-suppressant, the process comprising the steps of:

(a) mixing elemental sulphur, one or more H₂S-suppressants and optionally a filler in a mixing unit to obtain a mixture;

(b) shaping and/or pelletising the mixture obtained in step (a) in a pelletising unit to obtain H₂S-suppressant-containing sulphur pellets.

7. A process as claimed in claim 6, wherein the elemental sulphur is introduced as a slurry of sulphur particles in water, the particle size of the sulphur

particles preferably being between 0.5 and 150 microns, more preferably between 1.0 and 100 microns.

8. A process as claimed in claim 6, wherein the elemental sulphur is introduced as molten sulphur, the temperature of the mixture preferably being kept above 113 °C.

9. A process as claimed in any one of claims 6 to 8, wherein the H₂S-suppressant is one or more compounds selected from the class of free radical inhibitors and redox catalysts.

10. A process as claimed in any one of claims 6 to 9, wherein the pelletising unit is a drum granulator.

11. A process to manufacture a sulphur-containing asphalt paving mixture, the process comprising the steps of:

(i) preheating bitumen at a temperature of between 140 and 180 °C;

(ii) preheating aggregate at a temperature of between 140 and 180 °C;

(iii) mixing the hot bitumen with the hot aggregate in a mixing unit,

wherein sulphur pellets containing H₂S-suppressant according to any one of claims 1 to 5 are added either in step (i) or in step (ii) or in step (iii), preferably in step (iii).

12. A sulphur-containing asphalt paving mixture containing H₂S-suppressant, obtainable by a process according to claim 11.

13. Use of a sulphur-containing asphalt paving mixture containing H₂S-suppressant according to claim 12 in the paving of roads, wherein said paving mixture is applied to the road with a paving machine, followed by roller compaction until the required density has been reached.



A B S T R A C T

SULPHUR PELLETS CONTAINING H₂S-SUPPRESSANT

The invention provides sulphur pellets containing at least one H₂S-suppressant. The invention further provides a process for the manufacture of sulphur pellets containing at least one H₂S-suppressant.

The invention further provides a process for the manufacture of a sulphur-containing asphalt paving mixture using H₂S-suppressant containing sulphur pellets according to the invention.

The invention also provides the use of a sulphur-containing asphalt paving mixture comprising H₂S-suppressant in the paving of roads.

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/EP04/053357

International filing date: 08 December 2004 (08.12.2004)

Document type: Certified copy of priority document

Document details: Country/Office: EP
Number: 03257777.7
Filing date: 10 December 2003 (10.12.2003)

Date of receipt at the International Bureau: 03 February 2005 (03.02.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☐ BLACK BORDERS

☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES

☒ FADED TEXT OR DRAWING

☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING

☐ SKEWED/SLANTED IMAGES

☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS

☐ GRAY SCALE DOCUMENTS

☐ LINES OR MARKS ON ORIGINAL DOCUMENT

☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY

☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.